Development of Ripplon Scanning Technique for Surface Tension Mapping[1]

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ABSTRACT

In the case of semiconductor silicon single crystal growth process by the Czochralski method, it is considered that degradation of the crystal homogeneity may be caused by the distribution of surface tension at the melt surface, which promotes the Marangoni convection. However, conventional measurement techniques of surface tension such as sessile drop method cannot be applied for observation of this phenomenon, because the measurement has to be accomplished within short time and small spatial resolution *in situ* crystal growth process. In order to observe the distribution of the surface tension, we employed the surface laser-light scattering (SLLS) technique, which can measure the surface tension and the viscosity by observing propagation velocity and damping factor of the thermally excited microscopic capillary waves, called "ripplon". Ripplon scatters laser light focused on the liquid surface, and the scattered light is detected by the optical heterodyne interference technique. We have developed a new small and lightweight optical system (20mW, 532nm cw-YAG laser as a light source), which is attached on a scanning X-Y actuators (~300×300mm area). Preliminary mapping measurement has been performed with ethanol at room temperature in order to confirm the applicability of this technique.

KEY WORDS: Marangoni convection; ripplon; semiconductor silicon single crystal growth process; surface laser-light scattering technique; surface tension.

1. INTRODUCTION

Recently, it has been widely recognized that high quality single crystals of various substances are indispensable in many engineering fields. Especially, in the field of semiconductor production, silicon is one of the main substances because of the low manufacturing cost compared with other chemical compound materials such as GaAs, since it is easier to produce the semiconductor device made of silicon and silicon exists inexhaustible on the earth. The representative methods of silicon single crystal growth are the Czochralski (CZ) and floating zone (FZ) techniques. In the case of semiconductor silicon single crystal growth process by the Czochralski method, so far 8-inches diameter crystals have been widely utilized. In recent years, the manufacturing of 12-inches diameter crystals has already realized and 16-inches diameter single crystals will be widely utilized by the first quarter of 21st century in order to reduce the manufacturing cost of semiconductor devices. It is necessary to control heat and mass transfer at the melt/crystal interface in the crystal growth process. However, the manufacturing process of large diameter crystals has many unknown problems (e.g. accurate heat and mass transport phenomena in molten silicon), so it is difficult to produce large diameter crystals. As one of the unknown problems, there is the Marangoni convection that is created by distribution of surface tension. In the process of the single crystal growth by the Czochralski method, oxygen ooze out from the quartz crucible, and oxygen is transported by convection and diffusion. The large portion of oxygen evaporates from the melt surface, but small portion of oxygen is dissolved into single crystals. Very small concentration change of oxygen influences the quality of single crystals, and the Marangoni convection is caused by the concentration of oxygen in molten silicon, because the surface tension is sensitive with concentration of oxygen as well as temperature [1]. It is pointed out that the Marangoni convection influences the process of single crystal growth because it produces unknown heat and mass transfer. But a few researchers have been interested in the Marangoni convection as yet (e.g. The method to observe the tracer added to molten silicon with X-rays in micro gravity environment [1]), because many other factors may influence the process of single crystal growth and it is thought that the Marangoni convection affects smaller than the other factors (e.g. buoyancy convection [2]). In addition to the above-mentioned reasons, it is very difficult to observe the Marangoni convection directly outside micro gravity environment. Consequently, not only concrete influence of the Marangoni convection has not solved, but also observation of fixed quantitative behavior of the Marangoni convection has not been carried out at the present time. Therefore, in order to reveal the quantitative behavior of the Marangoni convection, we have developed the new apparatus to observe the distribution of the surface tension of molten silicon in the process of the Czochralski method.

Conventional methods to observe the surface tension of high temperature melts, such as sessile drop method or oscillating drop method using electromagnetic levitation [3], cannot be applied to observe the distribution of surface tension in the Czochralski configuration in the view of their measurement principles. Therefore, we have employed the surface laser-light scattering (SLLS) technique by observing propagation velocity of capillary waves, called “ripplon”, which can measure the surface tension and the viscosity at high sampling rate with a contact-free manner. Katyl and Ingard carried out the first SLLS experiment [4] and then SLLS is applied to measure liquid helium, silicon oil [5], water/ethanol mixture [6], and so on. In addition to observe the surface tension and the viscosity, SLLS has been applied to observe surface elasticity of langmuir films which are two-dimensional materials [7]. The measurement of the surface tension of high temperature melts (molten NaCl, molten silicon, molten $LiNbO_3$) in the temperature range up to 1770K by SLLS technique has been initiated by the authors’ laboratory [8-12]. Our idea so as to observe the distribution of the surface tension using SLLS technique is to scan the incident beam on a whole surface of molten silicon. We have developed a new small and lightweight optical system, which is attached on the scanning X-Y actuators.

Moreover, the new small and lightweight optical system of SLLS techniques may open a new paradigm not only to reveal the Marangoni convection, but also to use the value of the surface tension as one of the parameters in various manufacturing processes. As the first report, we describe the measurement theory of SLLS technique, outline of new experimental apparatus and result of preliminary measurement.

2. PRINCIPLE OF MEASUREMENT [9]

Ripplon is a very small wave on a liquid surface, which exists as long as not absolute zero degree temperature since thermal fluctuation promotes its movement.

The behavior of ripplon depends on the surface tension for restoration and the viscosity for damping. Typical wavelength of ripplon is smaller than several hundred micrometers and its amplitude is smaller than several nanometers. Ripplon can be described by the dispersion relationship [13], which is hydorodynamically deduced from Navier-Stokes equation and the equation of continuity. Hence, the dispersion relationship is solved under the following conditions.

(1) The amplitude of vibration is small enough compared with the wavelength of ripplon.

(2) Ripplon exists only on liquid surface.

(3) Action of ripplon depends only on surface tension for restoration.

(4) Action of ripplon depends only on viscosity for damping.

(5) The gravity is neglected, because wavelength of ripplon is small enough.

In the case of low kinematic viscosity liquid, the solution can be written as follows.

$$w_0{}^2 = \frac{s}{r} k^3 \tag{1}$$

$$\Gamma = 2\frac{h}{r} k^2 \tag{2}$$

Here w_0 is the angular frequency, s the surface tension, r the density, k the wave number, Γ the temporal damping factor and h the viscosity.

When the laser light irradiates on ripplon, the laser light is scattered by ripplon. In addition to the light scattering, the frequency of the laser light is shifted in proportion to the propagation velocity of ripplon as a result of the Doppler effect. The frequency of ripplon depends on wave number of ripplon, so we are able to extract particular wave number of ripplon to detect a scattered light having a particular scattered angle. However, the scattered light is very weak and frequency shift value is very small compared with the frequency of the incident light. Therefore, we have applied the optical heterodyne technique in the present study. The optical heterodyne technique is a method in which the frequency shifted light (scattered light) is mixed with the local oscillating light, we call “reference beam”, which is reflected light impinging on the liquid surface at an angle of several degrees with incident beam in order to extract particular scattered light, because the frequency of reflected light does not shift as a result of the Doppler effect. Principle of the measurement is shown in Fig. 1.

Because ripplon exists at random, the detected signals need to be applied to self-correlated equation in the time domain or Fourier transformation and averaging the signals in the frequency domain to make visible signals. Images of the signal at time domain and frequency domain are displayed in Fig. 2. We observe the signals in the frequency domain in the present measurement. It is possible to know the central frequency and the damping factor of the ripplon by the optical heterodyne technique and Fourier transformation. In order to calculate the surface tension and the viscosity, the damping factor and wave number is applied to the dispersion relationships, Eqs. (1) and (2).

3. EXPERIMENTAL APPARATUS

In principle, it is possible to estimate the Marangoni number at least by measuring the difference of the surface tension between two points on a surface simultaneously. Therefore, the simplest idea of construction of our target apparatus may be multiple fixed probe laser beams impinging on the molten silicon surface. The purpose of the present study, however, is to measure the degradation of surface tension, not to measure the accurate absolute value. Consequently, we have decided to develop a new small and lightweight optical system and to mount the system on a X-Y actuators to scan whole molten silicon surface within a short enough time. Our idea is to make “equi-surface tension line” similar to contour line or isobar. The objective specifications of the new apparatus are

(1) The distances of each scanning points are less than 10 mm matrix on an entire liquid surface.

(2) Sampling time is less than 1s per single point.

(3) Whole scanning time is within several minutes.

Fig. 3 shows the concept of the entire scanning system. The overall structure of the optical system is shown in Fig. 4. In order to satisfy the above specifications, we have adopted a single mode 20mW-532nm-cw-YAG laser (model: 58 GCS 421 MELLES GRIOT) as a laser source, because of its high coherency and lightweight. A pair of convex and concave lenses (L1 and L2 in Fig. 4) are installed to suppress the spread angle of the laser beam and to focus the laser beam on the liquid surface. The distance between convex and concave lenses can be changed by using linear stage (stroke; 6mm) in order to adjust the focal distance to a liquid surface from 1000 mm to 3000 mm depending on geometrical configurations of various applied systems. We have adopted a polarizing beam splitter (PBS in Fig. 4) to split the laser beam between incident beam and reference beam. PBS splits the laser light into about 98% and 2% in intensity. Strong beam is used as an incident beam and weak beam is used as a reference beam. If the reference beam is not weak enough, we adopt a neutral density filter (ND filter in Fig. 4) to weaken the reference beam suitable for the optical heterodyne detection. In order to determine the wave number of ripplon, we have adopted the method that is to measure the distance between incident beam and reference beam with laser beam analyzer near and far points from the liquid surface, and calculate the angle from geometrical configuration as shown in Fig. 5. The error due to the wave number determination by this method is estimated to be about ±1.3% at $k = 1\times10^5 \mathrm{m}^{-1}$ which corresponds to 1000mm distance between the mirror and the liquid surface.

The scattered light with the reference beam is detected by a photomultiplier tube (PMT). The detected signals go through an amplifier and a high pass filter to cut the noise at low frequency region. We have designed the optical system small and lightweight to mount on the X-Y actuators (300×300mm stroke). As a result, we have succeeded to develop 3kg optical system on a 170×220mm optical surface plate.

4. PRELIMINARY MAPPING MEASUREMENT

In order to confirm that the present apparatus can be applied to the surface tension mapping measurement, we have employed ethanol at room temperature. At first, we have measured the surface tension of ethanol at fixed point to check the instrument is working properly in accordance with the theory. The measured spectrum of the ripplon at three different wave numbers is shown in Fig. 6. Fig. 6 indicates the expected dependence of w_0 vs. k descried by Eq. (1).

In the next, we have attempted to scan the laser beam on the liquid surface into 10mm matrix as shown in Fig. 7. At each point on the surface, we have repeatedly measured surface tension ten times, and then moved to the next point. In this way, the preliminary surface tension mapping measurement has been performed within about seven minutes. The obtained mapping result is presented in Fig. 8. The difference among the measured surface tensions is obviously larger than the reproducibility at each point. Although, at the present time, we are not able to discuss the result in Fig. 10, this is the first attempt to observe the surface tension distribution by using the surface laser-light scattering technique.

5. ACKNOWLEDGMENTS

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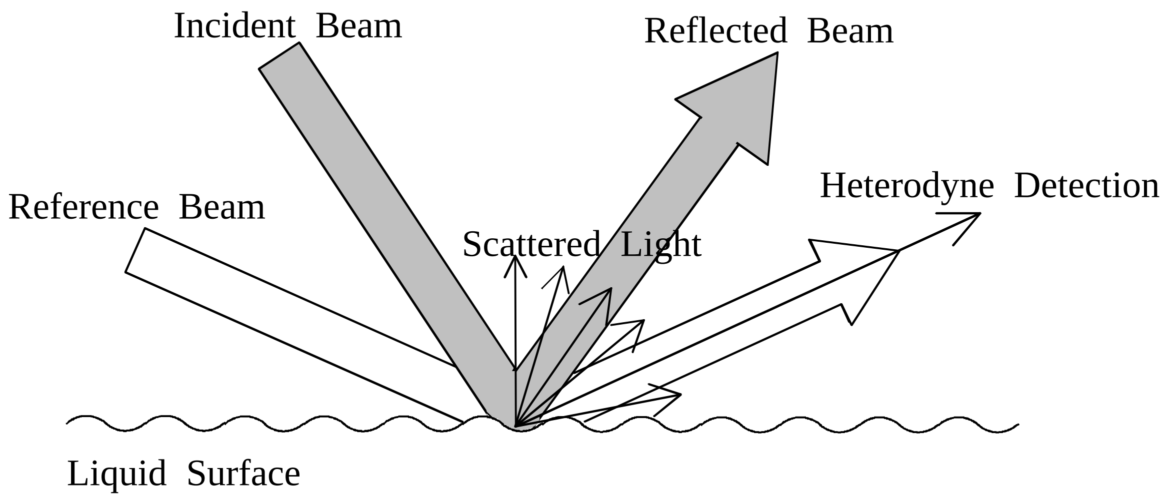
LIST OF FIGURE CAPTIONS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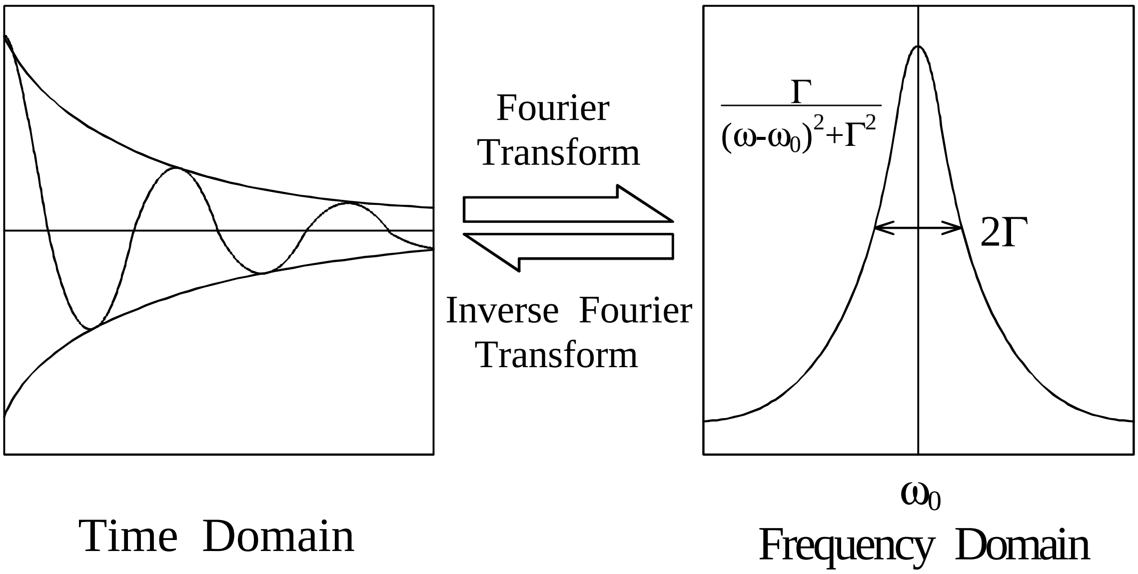
Reflected Beam
Heterodyne Detection
Reference Beam
Scattered Light
Liquid Surface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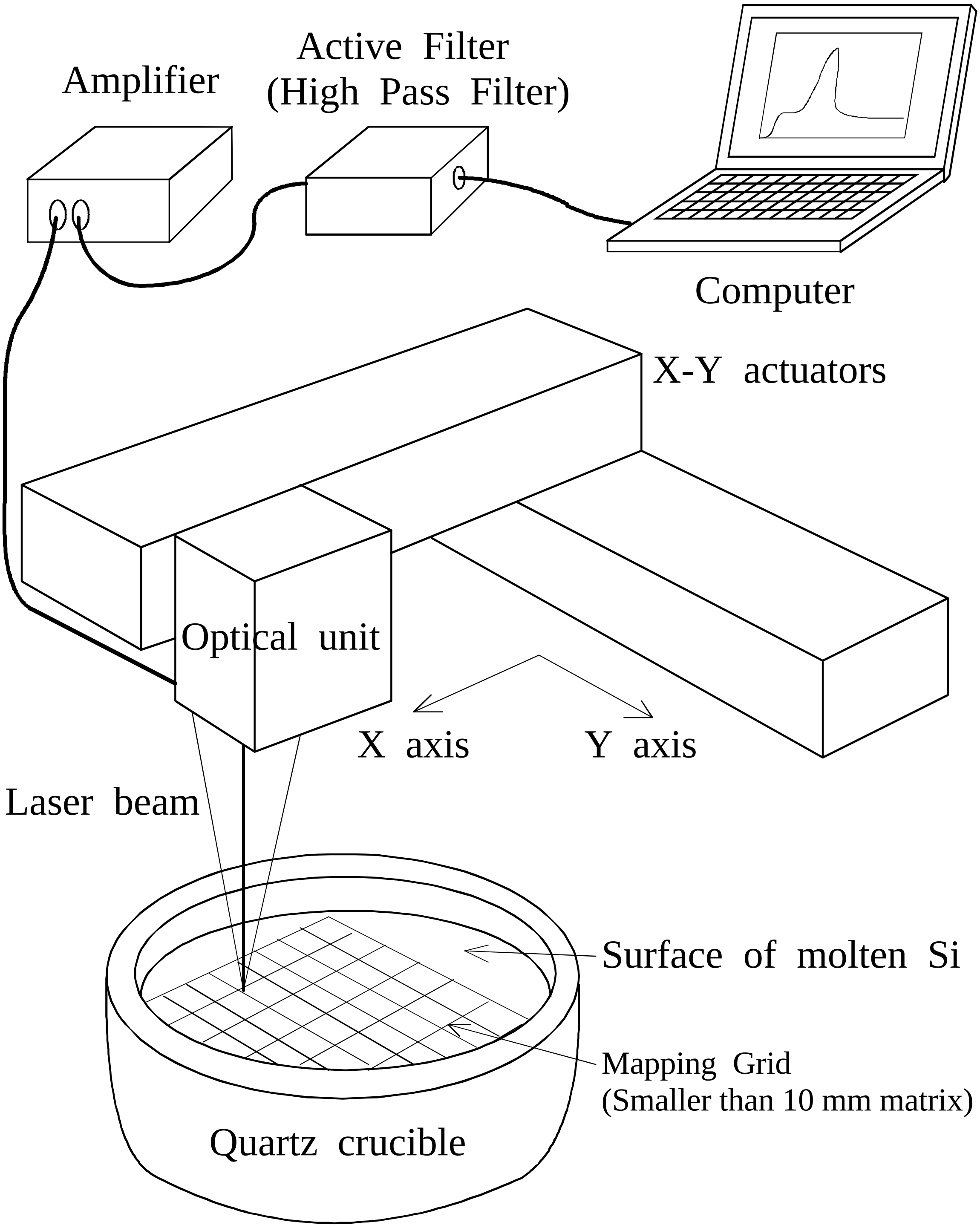
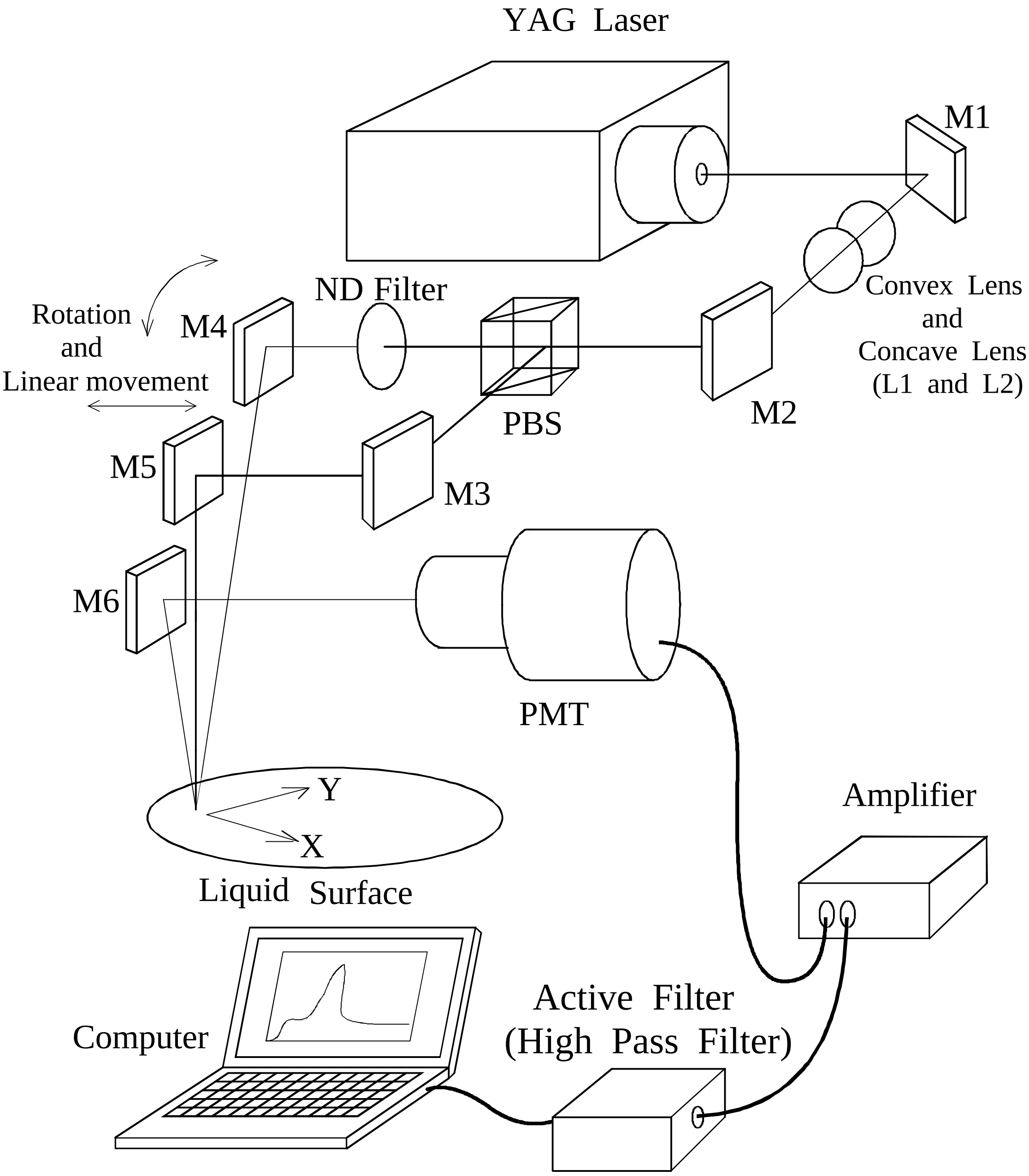
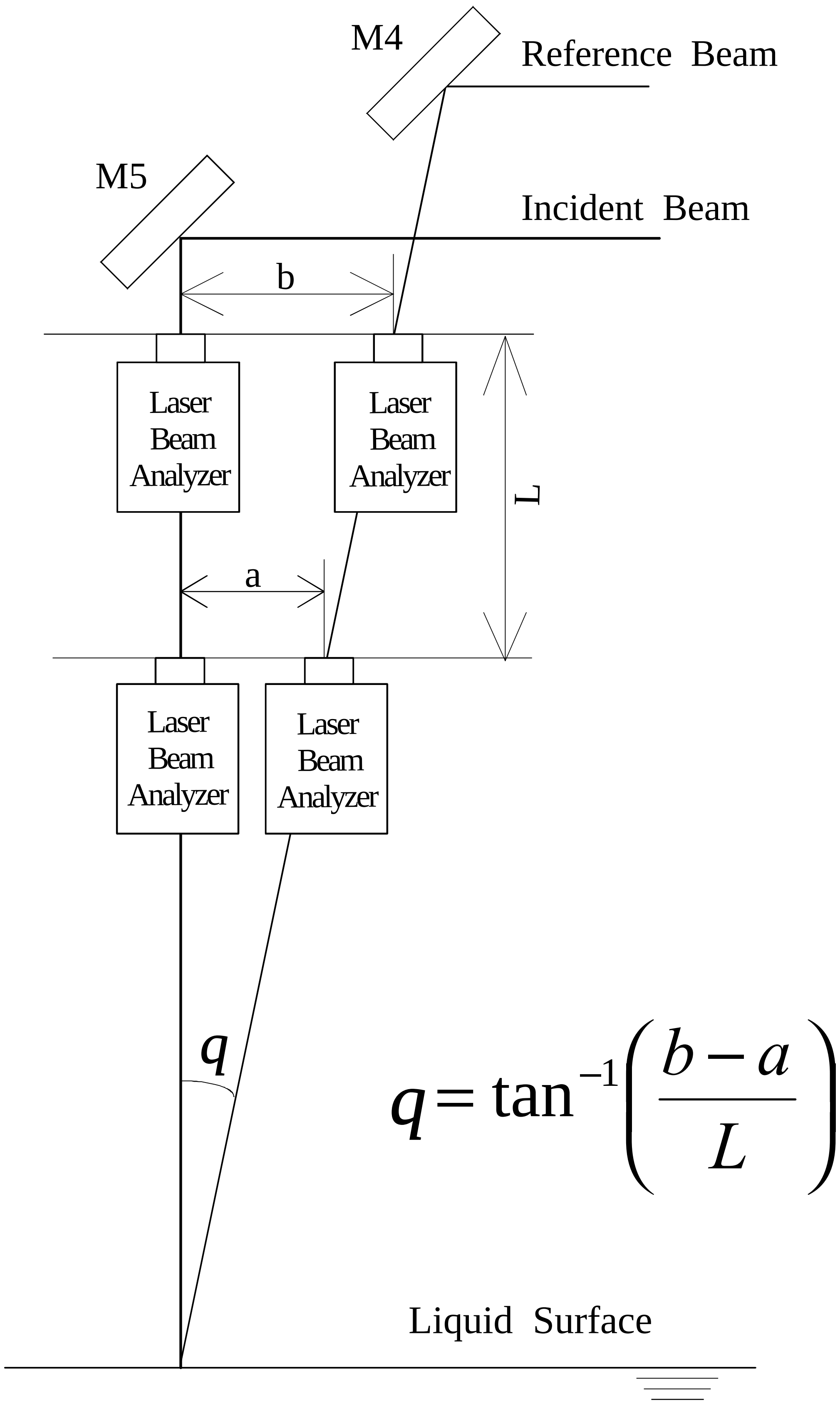
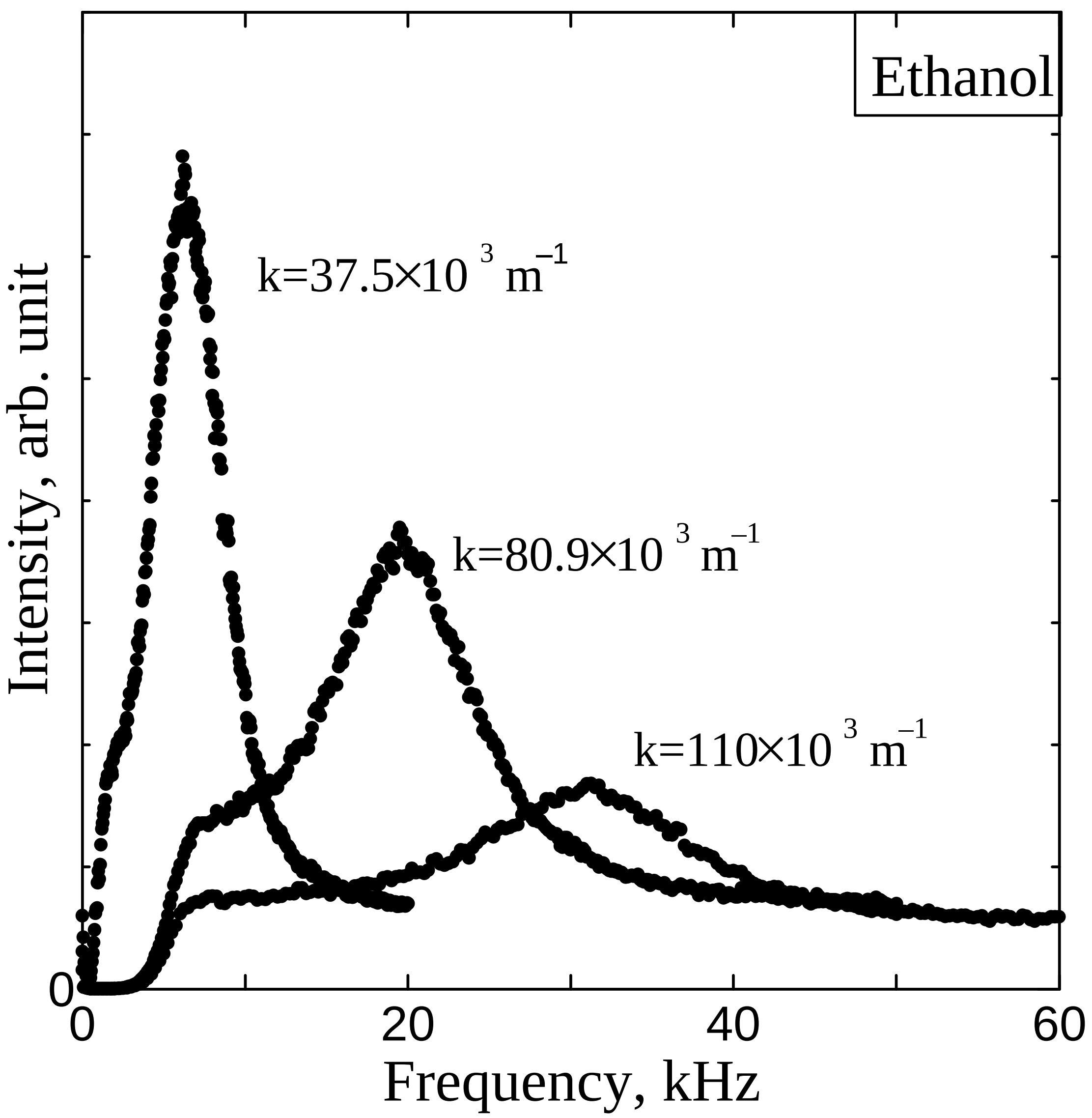
Transform
Inverse Fourier
Transform
$\frac{\Gamma}{(\omega-\omega_0)^2+\Gamma^2}$
2Γ
ω_0
Time Domain
Frequency Domain


Amplifier
Active Filter
(High Pass Filter)
Computer
X-Y actuators
Optical unit
X axis
Y axis
Laser beam
Surface of molten Si
Mapping Grid
(Smaller than 10 mm matrix)
Quartz crucible

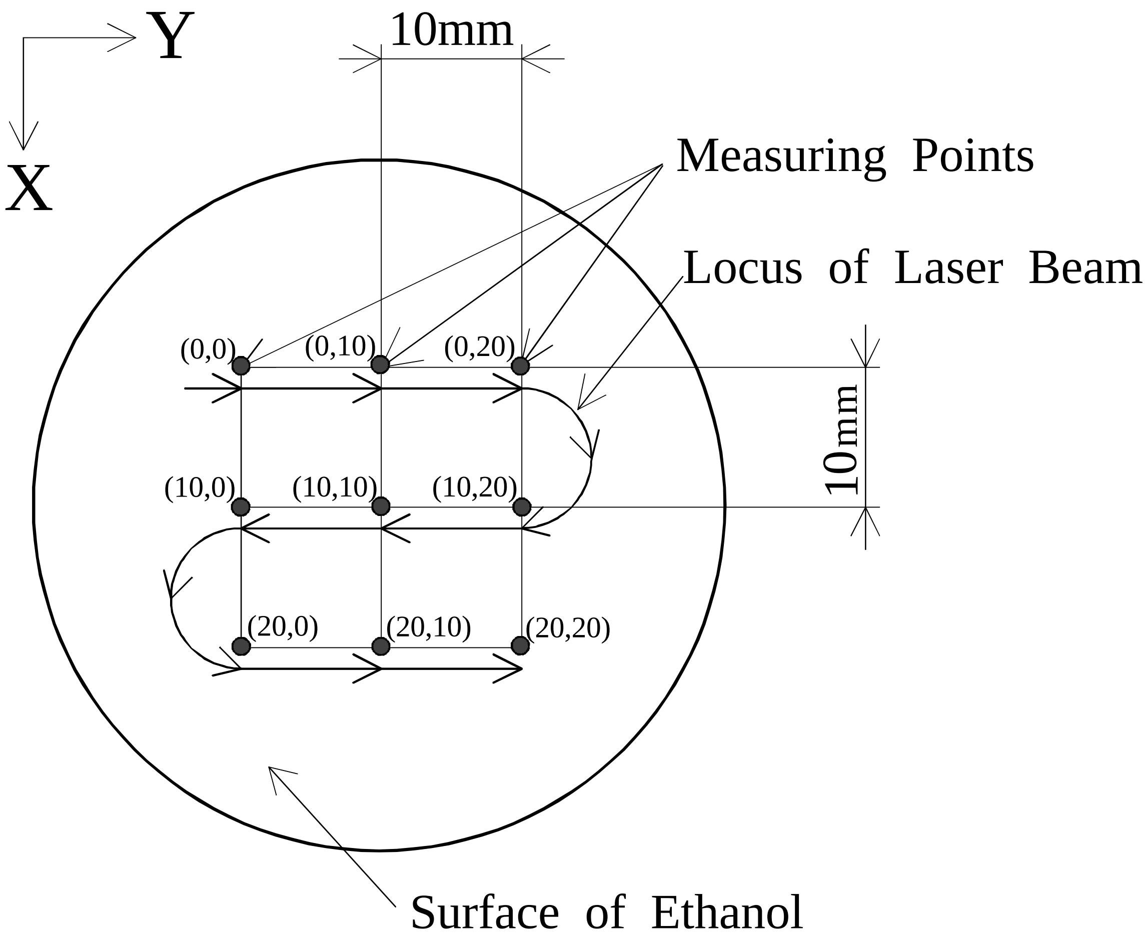

YAG Laser
M1
Convex Lens
and
Concave Lens
(L1 and L2)
ND Filter
Rotation
and
Linear movement
M4
PBS
M2
M5
M3
M6
PMT
Y
X
Liquid Surface
Amplifier
Computer
Active Filter
(High Pass Filter)

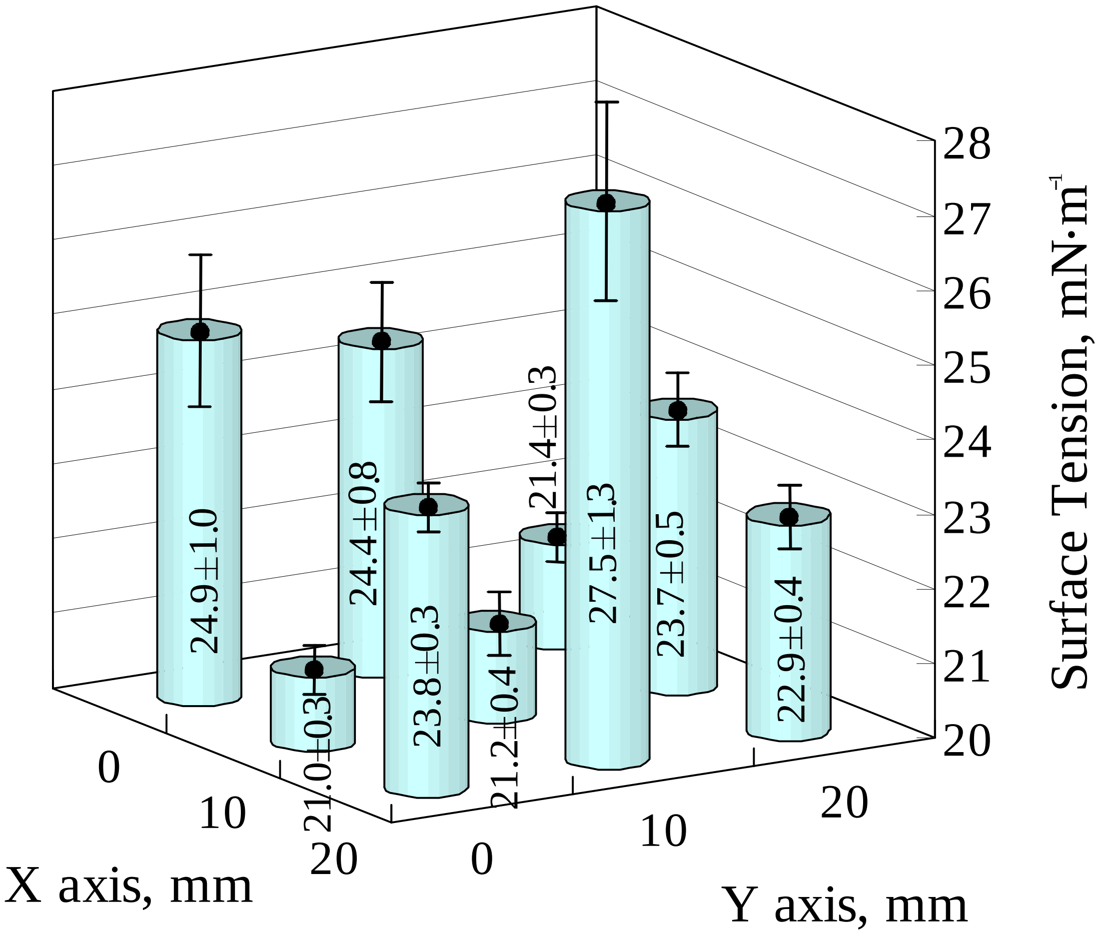


$$q = \tan^{-1}\left(\frac{b-a}{L}\right)$$



Ethanol
k=37.5×10 3 m–1
k=80.9×10 3 m–1
k=110×10 3 m–1
Intensity, arb. unit
0
0
20
40
60
Frequency, kHz


Y
X
10mm
Measuring Points
Locus of Laser Beam
(0,0)
(0,10)
(0,20)
(10,0)
(10,10)
(10,20)
(20,0)
(20,10)
(20,20)
10mm
Surface of Ethanol



28
27
26
25
24
23
22
21
20
Surface Tension, mN·m-1
24.9±1.0
24.4±0.8
21.0±0.3
23.8±0.3
21.2±0.4
21.4±0.3
27.5±1.3
23.7±0.5
22.9±0.4
0
10
20
X axis, mm
0
10
20
Y axis, mm